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Competitive Binding of Protons and Metal Ions in Humic Substances by Lanthanide Ion Probe Spectroscopy

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Competitive Binding of Protons and Metal Ions in Humic Substances by Lanthanide Ion Probe Spectroscopy

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A pH-dependent, continuous, multiligand model is described. It is based on the Gaussian distribution model, which has been used to describe both proton binding by humic substances as well as metal binding by humic substances. However, the Gaussian distribution model has never been used to describe the competitive binding of the metalated and protonated ligand species. The inclusion of pH dependence should allow one to predict metal binding constants that are more representative of the true thermodynamic binding constants rather than curve-fitting parameters with no chemical significance.

INTRODUCTION

An understanding of metal–humic interactions is important from an environmental viewpoint, and research advances have been the subject of several recent review articles (*1–4*). A more thorough understanding of the interactions between metals and humic substances is necessary in order to predict the environmental fate of these metals and their complexes. This requires the development of both analytical methodology and mathematical models to facilitate the necessary distinction between complexed and free metal ions.

In a recent paper (*5*), we reported on the development of a spectroscopic technique designed to probe metal binding sites of humic substances. This spectroscopic technique was based on the unique fluorescence properties of the trivalent europium ion, Eu^{3+}. We demonstrated that the fluorescence spectrum of the probe metal ion was sensitive to the ligation of the metal ion with humic material. The sensitive nature of the fluorescence measurements permitted the detection of metal–humic complexation at humic material concentrations found in the environment.

In this paper, we utilized the Gaussian distribution complexation model to describe the speciation reactions between Eu^{3+} and Suwannee River fulvic acids. This continuous multiligand model was based on the assumption that complex humic substances contain a large number of nonidentical ligand sites that are normally distributed about an average or mean log K_{Mi} value, where K_{Mi} is the complex formation constant. The Gaussian distribution model was initially developed by other researches (*6–9*) to describe proton binding by humic materials. In other cases where this model has been used to describe metal binding by humic acids (*8, 9*), including our recent application (*5*), the inherent competition between protons and the metal ions for the same set of ligand sites was ignored. As a result of the neglect of competitive binding, this model predicts *conditional* binding constants of the metal of interest. Since conditional binding constants are only constant at constant pH, different sets of experimental data measured at a different pH value cannot be fitted with same set of parameters.

In this paper, we report the effect of pH on metal–humic complexation from a true competitive reaction point of view. The inclusion of the pH dependence into the previously described Gaussian distribution model allowed us to predict the average binding constant (μ_M) of the fluorescent probe metal ion and the standard deviation of this average log K_{Mi} value (σ) which is representative of the width of the ligand distribution. These predicted values of μ_M and σ are more representative of true thermodynamic constants, regardless of pH. This model is more realistic continuous-multiligand model that better describes metal–humic interactions. It should also be emphasized that the method is an equilibrium method and not a kinetic method for determining trace-metal binding constants.

EXPERIMENTAL SECTION

Instrumentation. The instrumentation, optical configuration, and the preparation of the Suwannee River fulvic acid (*10*) samples have been described elsewhere (*5*). In these metal–humic titrations, the europium concentrations typically ranged from 1×10^{-2} to 1×10^{-6} M and the fulvic acid concentrations were held constant at 10 ppm. The relative concentrations of the titrant and the fulvic acid assured a wide range of coverage of the metal binding sites with Eu^{3+} ions.

THEORY

The theory and principles regarding the implementation of the lanthanide ion probe have been discussed previously (*5*); therefore, only a brief review will be given. As was previously mentioned, the fluorescence spectrum of the probe metal ion is sensitive to ligation of the metal ion with humic substances. The sensitive nature of these spectra is due to the existence of a hypersensitive transition that is common to lanthanide ions. Hypersensitive transitions are emissive transitions of the lanthanide ion that are sensitive to ligation.

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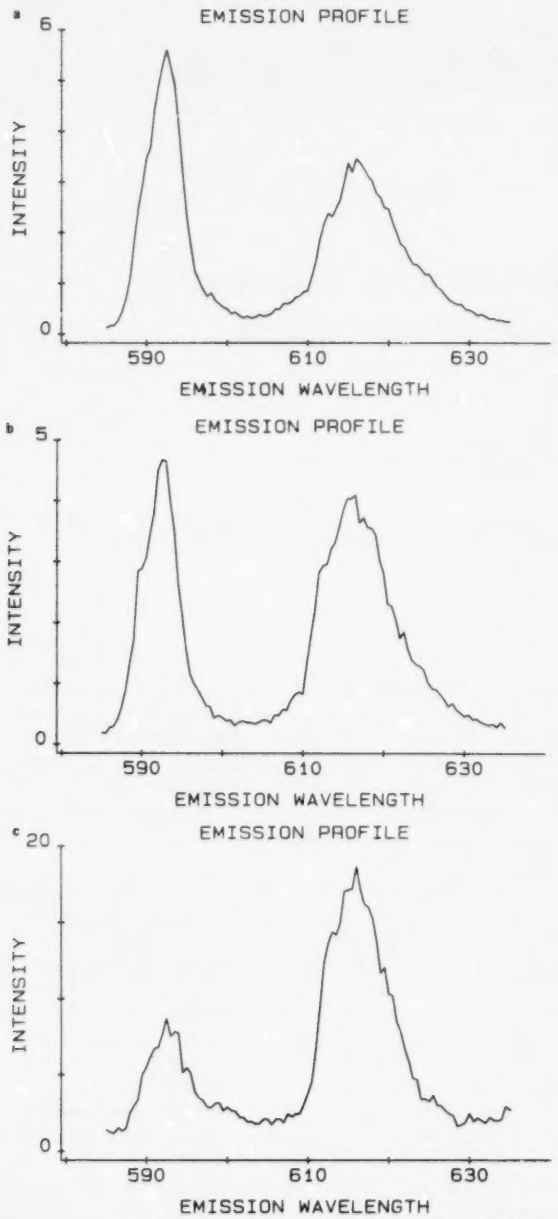

Figure 1. (a) Emission spectrum of 5×10^{-2} M Eu^{3+} and 100 ppm Suwannee River fulvic acid. The excitation wavelength was 394.3 nm and the pH of the solution was 3.5. (b) Emission spectrum of 2.5×10^{-3} M Eu^{3+} and 100 ppm Suwannee River fulvic acid. The excitation wavelength was 394.3 nm and the pH of the solution was 3.5. (c) Emission spectrum of 5×10^{-5} M Eu^{3+} and 100 ppm Suwannee River fulvic acid. The excitation wavelength was 394.3 nm and the pH of the solution was 3.5.

The hypersensitive transition of the Eu^{3+} ion occurs at 616 nm (*11*). The effect of the hypersensitive transition is illustrated in Figure 1. Three different emission profiles of the Eu^{3+} are shown. For each, the concentration of metal ion was varied, but the humic concentration remained constant. At very large values of C_M/C_L (where C_M is the total concentration of metal and C_L is the total concentration of ligand), the majority of the metal is free (aquo) ion and the corresponding fluorescence spectrum is representative of the free metal ion. For the case of the free metal ion, the intensity of the hypersensitive transition is not enhanced. If μ_M is large enough, at very small values of C_M/C_L, the majority of the metal M is bound and the intensity of the hypersensitive transition in the corresponding spectrum is enhanced relative to the nonhypersensitive band. This effect is a continuous function of the metal ligation and is assumed constant for all acidic sites of the humic substance. Theories and mechanisms of the hypersensitive transitions have been discussed by Mason et al. (*12*).

The ratio of the integrated peak intensity of these bands is

$$R = I_{592}/I_{616} \tag{1}$$

Plotting R as a function of logarithm of the total metal, log C_M, yields a sigmoidal shaped curve. This plot, can be viewed as a spectral titration curve. We have shown in our previous report (*5*) that the intensity ratio R was mathematically related to the concentrations of the bound and free metal species.

This mathematical relationship was derived previously and [M], the concentration of the free metal ion, is given as

$$[M] = \frac{C_M^*(X_b - R^*X_b/X_s)}{R^*(1 - X_b/X_s)} \tag{2}$$

where X_b is the observed value of R in the absence of any humic material and X_s is the observed value of R at the minimum limiting condition where all Eu^{3+} ions are bound to the humic sites. The values of X_b and X_s were experimentally measured. Because the expression for [M] is related to $\sum[ML_i]$ through the mass balance equation of C_M, the total bound metal can be expressed as

$$\sum[ML_i] = C_M - [M] \tag{3}$$

This mathematical analysis of the experimental data provided the means to determine quantitatively the concentrations of the bound and free metal species at any point during the titration process.

CONTINUOUS MULTILIGAND pH DEPENDENT MODEL

To facilitate the incorporation of the effects of ionization of the humic substance into the previous single-species, pH-independent model, it was assumed that two distinct distributions for the competitive species, protons and metal ions, exist for a single population of humic ligands. Both distributions are Gaussian in nature and differ only by a constant displacement of the log K_i values. The widths of these distributions (σ) remained constant for both species. This assumption implies that the ratio of K_{Mi}/K_{Hi} is constant, where K_{Hi} is the proton binding constant at sites of type i and K_{Mi} is the binding constant for the metal at sites of type i.

With this assumption in mind, the objective of the following derivation was to develop an expression for $[ML_i]$ in terms of all previously known variables, including [H] and K_{Hi}. In our previous application of the Gaussian distribution model, the complexation reaction for single metal–humic interaction, where a 1:1 stoichiometric concentration of metal (M) and ligand (L) was assumed, was written as

$$M + L_i \leftrightarrow ML_i \tag{4}$$

The formation constant K_{Mi} was written as

$$K_{Mi} = \frac{[ML_i]}{[M]\,[L_i]} \tag{5}$$

In its final form, the generalized chemical equilibrium equation, that was representative of the single-species, pH-independent model was expressed as

$$[ML_i] = \frac{K_{Mi}^*[M]^*C_i}{1 + K_{Mi}^*[M]} \tag{6}$$

where C_i is the concentration of the binding site of type i.

Similar to eq 4, the protonation reaction for sites of the type i can be written as

$$H + L_i \leftrightarrow HL_i \quad (7)$$

The formation constant K_{Hi} is

$$K_{Hi} = \frac{[HL_i]}{[H][L_i]} \quad (8)$$

where $[HL_i]$ is the concentration of the protonated sites of type i and [H] is the concentration of the proton. The ratio of the two formation constants (K_{Mi} and K_{Hi}) can be expressed as

$$\frac{K_{Mi}}{K_{Hi}} = \frac{[ML_i][H]}{[M][HL_i]} \quad (9)$$

The protonated ligand, $[HL_i]$, is difficult to measure; therefore, it should be expressed in other terms. From the mass balance equation of the binding sites of type i, $[HL_i]$ can be written as

$$[HL_i] = C_i - [ML_i] - [L_i] \quad (10)$$

and from eq 5 $[L_i]$ can be expressed as

$$[L_i] = \frac{[ML_i]}{K_{Mi}^*[M]} \quad (11)$$

Following the successive substitutions of the above expression of $[L_i]$ into eq 10 and the expression of $[HL_i]$ into eq 9, followed by simplification and final rearrangement, an expression for $[ML_i]$ is written as

$$[ML_i] = \frac{K_{Mi}[M]C_i}{1 + K_{Mi}[M] + K_{Hi}[H]} \quad (12)$$

The only difference between the final expression of $[ML_i]$ shown above and the expression for $[ML_i]$ for the single metal–pH independent model (eq 6) is the additional term ($K_{Hi}[H]$), found in the denominator. The inclusion of this term accounts for the inherent competition of the protons and the probe metal ions. This generalized expression can be made more specific as needed. In the continuation of our metal–humic complexation studies, we have applied this general competitive species (protons and metal ions) chemical equilibrium model to the Gaussian distribution complexation model.

The Gaussian distribution model yields the following expression for the ligand distribution (*8*, *9*):

$$C_i = \frac{C_L}{\sigma(2\pi)^{1/2}} \exp\left[-\frac{1}{2}\left[\frac{\mu - \log K_i}{\sigma}\right]^2\right] d \log K \quad (13)$$

where C_i is the concentration of the ligand of type i, C_L is the total concentration of carboxylic ligands of the humic substance, μ is the mean log K_i value of the sites of type i, and σ is one standard deviation of the mean binding constant. Note that eq 13 is written in a general form, i.e. without using subscript M or H.

This expression for C_i was substituted into eq 12. Solutions to this equation yield the concentrations of the bound metal at a single binding site i ($[ML_i]$). The objective in this modeling exercise is to compare the calculated values of the bound metal concentrations with the experimental values of the total bound metal concentrations obtained from the analysis of europium emission spectra. In order to facilitate the comparison of the calculated values, $[ML_i]$, and the observed values, $\sum[ML_i]$, these two expressions must parallel each other. Therefore, it is necessary to sum eq 12 over all i values to obtain an expression for the total bound metal, $\sum[ML_i]$. This summation is expressed as the following integral:

$$\sum_i[ML_i] = \frac{C_L}{\sigma(2\pi)^{1/2}} \int_{-\infty}^{+\infty} \frac{K_{Mi}[M]}{1 + K_{Mi}[M] + K_{Hi}[H]} \times \left[-\frac{1}{2}\left[\frac{\mu_M - \log K_{Mi}}{\sigma}\right]^2\right] d \log K_M \quad (14)$$

The solutions to this integral provided expressions for the total bound metal according to the pH-dependent Gaussian model. It is similar to the final expression derived for the pH-independent model, where the modeling parameters μ_M and σ are characteristics of the humic materials and represent the mean binding constant of Eu^{3+} and the breadth of the distribution of the binding sites, respectively. The additional $K_{Hi}^*[H]$ term in the denominator, however, denotes the humic acid ionization and the competition of protons and metal ions for the available binding sites. Initial guesses for the modeling parameters μ_M and σ are provided. The integral limits are set to $\pm 4\sigma$, and this expression is numerically evaluated. For each individual calculated K_{Mi} value, the corresponding K_{Hi} value is known through the initial assumption that K_{Mi}/K_{Hi} remains constant over all i values. The value of this constant was taken to be the ratio of $10^{\mu_M}/10^{\mu_H}$ where μ_M was taken to be the mean binding constant of europium ion and μ_H was the mean binding constant for proton. The value of μ_H was taken to be 4.0. The value of [H] was estimated from the measured pH. The modeling parameters μ_M and σ were fitted by means of the previously described least-squares fitting routine (*5*).

Prior to the discussion of the experimental results in this study, we have chosen to illustrate the effects of competitive binding of the hydrogen ion and the probe metal ion according to this pH-dependent model with aid of a computer-simulated speciation study. The relative distributions of the various ligand species are shown in Figure 2 as a function of pH. The outer curve in each figure is representative of the entire C_i ligand distribution; therefore, by definition, the three individual ligand species (protonated ligands, metalated ligands, and free ligands) are subspecies of this distribution. The distributions of these various species have been plotted as concentration of C_i vs site number. The relative distributions of the individual ligand species are of course dependent on the values of C_L, C_M, pH, μ_M, and μ_H. In each figure, all values were held constant with the exception of pH. The result of varying the pH illustrates the competitive binding nature of the hydrogen ion. In figure 2, the total metal concentration is held constant at 1×10^{-4} M. The different proton concentrations 1×10^{-2}, 1×10^{-3}, 1×10^{-4}, and 1×10^{-5} M result in a significantly altered distribution of the various ligand species. The protonated ligand species dominate the distribution at a pH of 2.0. The protons are preferentially bound to the stronger sites, indicated by the skewed Gaussian curve. The metalated ligand species are also present but at smaller concentrations. Even though free binding sites are still available, the metal ions are also preferentially bound to the same stronger ligand sites. The remaining free ligand sites, represented by the L_i distribution curve, are recognized as weaker binding sites of the C_i distribution, i.e. located at the left-hand side in the C_i distribution. As the proton concentration is decreased (pH is increased from 2.0 to 3.0), the concentration of the protonated ligand species decreases and the concentration of the metalated ligand species increases. The metalated ligand species dominate the distribution at pH 5.0. These distribution curves illustrate that protons and metal ions are truly competitive species that compete for the same set of binding sites.

RESULTS AND DISCUSSION

The conclusions drawn from the previous simulation study via the ligand distribution curves indicated that as the concentration of hydrogen ion was increased, a smaller percentage

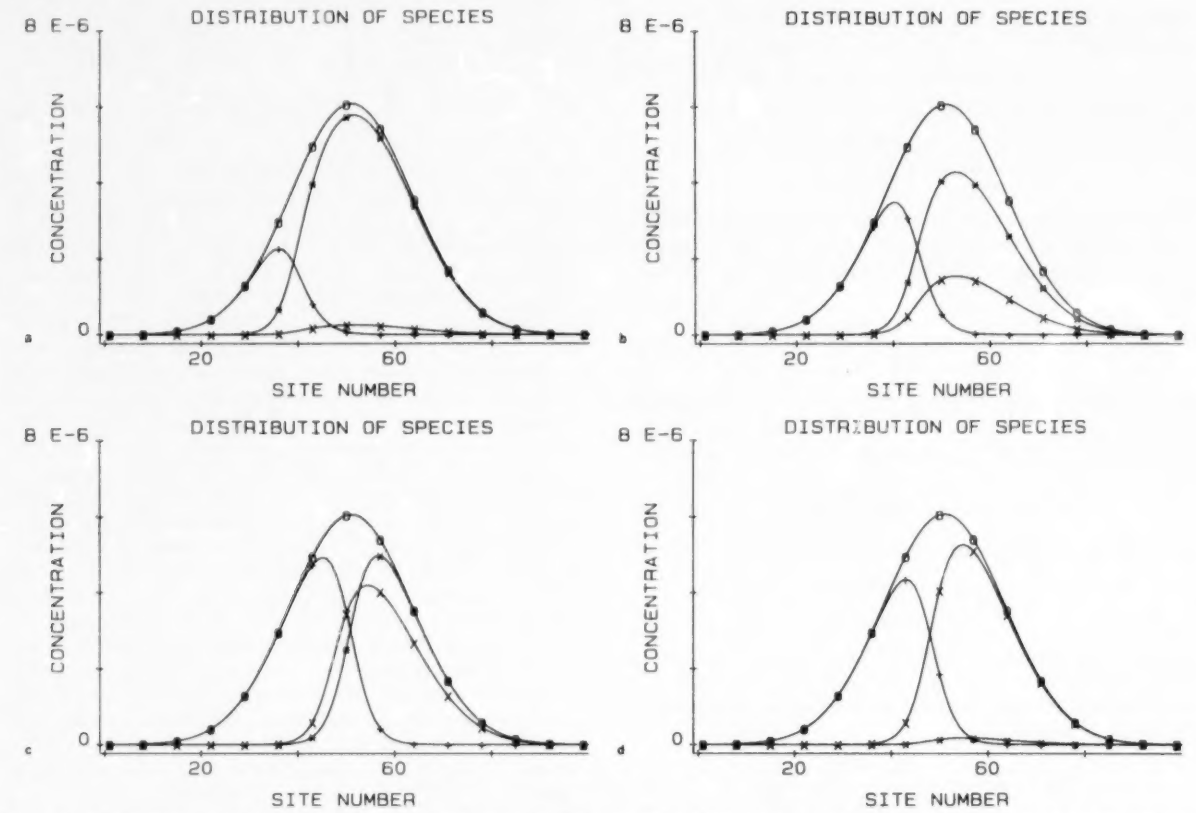

Figure 2. Distribution curves of various ligand species to illustrate the competitive binding nature of the proton and the metal ion. The pH was varied from 2.0 to 5.0 and the concentration of Eu^{3+} ion was held constant at 1×10^{-4} M: (a) pH = 2.0, (b) pH = 3.0, (c) pH = 4.0, (d) pH = 5.0; (O) total ligand distribution, (•) protonated ligand distribution, (×) Eu^{3+} metalated ligand species, (+) free ligand species.

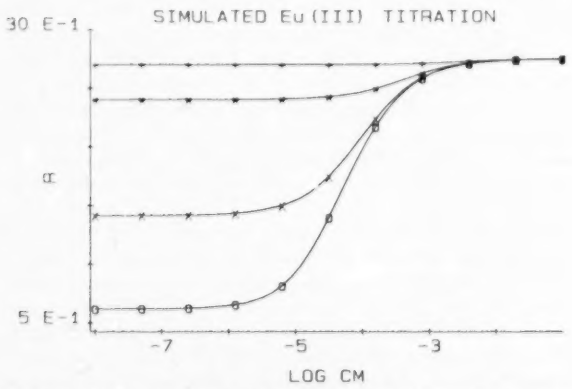

Figure 3. Computer-simulated fulvic acid and Eu^{3+} titration curves at various pH values: (O) pH = 5.0, (×) pH = 4.0, (•) pH = 3.0, (+) pH = 2.0.

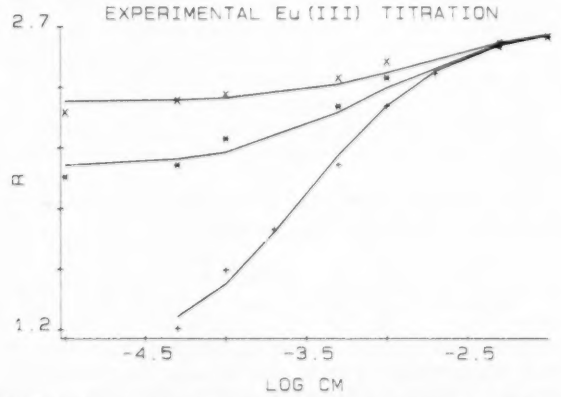

Figure 4. Experimental and calculated Eu^{3+} and Suwannee River fulvic acid titration curves, R vs log C_M, as predicted by the pH-dependent continuous multiligand model: (×) pH = 2.5, (•) pH = 3.0, and (+) pH = 3.5; 10 ppm FA.

of the total metal was bound. In parallel with this simulation study, displacement of the probe metal ion should be readily observable in a Eu^{3+}–humic titration experiment. We were able to predict the results of the titration curves, R versus log C_M, via another simulation study according to the pH-dependent model. The results of this pH simulation study are illustrated in the Figure 3. As the pH is decreased from 5.0 to 2.0, a larger percentage of the Eu^{3+} is displaced due to the larger concentration of the competing hydrogen ion. Therefore, for a given C_M value, the intensity ratio values R (I_{592}/I_{616}) increase, indicating that less of the total Eu^{3+} ion is bound.

The Eu^{3+} metal titrations of the Suwannee River fulvic acids were performed at pH 2.5, 3.0, and 3.5. The experimentally observed and calculated titration curves, R versus log C_M, are shown in Figure 4. The calculated curves were fitted to the experimental results with a best fitted μ_M value of 4.4 and a σ value of 2.17. The measure of the binding constant of the most probable site in the ligand distribution (μ_M) and the width of the distribution (σ) were *constant* for each titration.

The pH-dependent model predicted larger values for both fitting parameters, μ_M and σ, than the previous pH-independent model (*5*), 4.5 vs 3.5 and 2.17 vs 1.1, respectively. The interaction between the protons and the binding sites changes both the effective complex formation strengths of the binding sites and the effective width of the binding sites distribution.

The higher the proton concentration, the weaker the effective complex formation strengths, and the narrower the effective width of the Gaussian distribution representing the humic materials. This can be explained as follows: at low pH, before titration even begins, a significant portion of the binding sites are already occupied by the protons. The Eu^{3+} ions need to compete with the protons in order to form each and every ML_i complex molecule. Relative to the case where the existence of protons can be neglected, it is obvious that in order to occupy all of the binding sites, more metal ions are needed. This implies that if the existence of protons is neglected, while in reality they exist independent of the model being used, then the metal ions Eu^{3+} appear to be more weakly bound or μ_M appears to have a smaller value than it should be. Similar rationalization can be used to explain why the presence of competing protons makes the distribution of the binding sites appear narrower. During the titration some of the binding sites, preferentially the stronger sites, are occupied by the protons and are less available to Eu^{3+} and therefore make the effective width of the binding site distribution appear to be narrower.

Consequently, when this mathematical model was applied to the experimental results of identical humic substance materials, the predicted values for both modeling parameters, μ_M and σ, were greater than previous predictions obtained from the pH-independent model (*5*). The predicted values of the modeling parameters obtained from the pH-dependent model were *constant*, whereas the modeling parameters predicted by the pH-independent model were conditional and related directly to pH.

Because the initial pH-independent model predictive lower values for μ_M and σ, we proposed a simple test which verified that the results obtained from that study were correctly biased in the direction of lower μ_M and σ values. This test consisted of creating a set of computer-generated R values (where $R = I_{592}/I_{616}$), via a computer program based on the pH-dependent, Gaussian distribution model discussed in this paper. These data were generated at constant pH and at predetermined values of the curve fitting parameters μ_M, σ, and C_L. These plotted data represented the titration curve of a noiseless data set. The absence of any noise in the data of course allowed the fitting programs to fit the modeling parameters μ_M and σ exactly. The initial value of μ_M and σ that were used to generated the data were 4.5 and 2.17. These values were used since they corresponded to the best fitted results of the actual experimental data. This set of computer-generated data was then submitted to the original pH-independent model and the modeling parameters, μ_M and σ, were fitted. The result of fitting the same data to the pH-independent modeling program lowered these values of μ_M and σ to 3.5 and 0.55. After several attempts, the pH-independent modeling technique consistently lowered both parameters. Both experimental and simulated data resulted in lower values for μ_M and σ when subjected to the initial pH-independent modeling routine.

A number of models have been used to model the proton or metal titration characteristics of humic substances. Cabaniss and Shuman (*13*) measured and modeled cupric ion binding in Suwannee fulvic acids as a function of pH and other chemical parameters. A discrete multisite model (*3*, *14*) of binding sites was used. The presence of five types of binding sites was used to fit the experimental data. Five pairs of C_i and K_{Mi} values were produced. The C_i values were not constant among titrations at the same C_L but different pH. Consequently, data from different pH values could not be fit with one set of parameters, indicating that the parameters were conditional and not thermodynamic constants. While the Gaussian model assumes an infinite number of types of sites, these sites are described by only three parameters: the

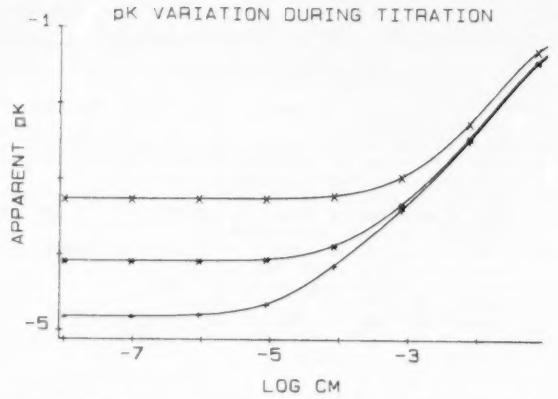

Figure 5. Variation of apparent pK during titration at different pH values: (X) pH = 2.5, (*) pH = 3.5, and (+) pH = 4.5.

center of the distribution, μ_X (where X denotes proton or any metal ions that bound to the humic sites), the width of the distribution, σ, and the total binding capacity for all sites C_L.

Other workers, Marinsky et al. (*15–17*), modeled Cu^{2+} and Eu^{3+} binding by fulvic acids using an electrostatic polymer model. The model is based on the assumption that the chemistry of humic substances is similar to that of polymers and attempts to include Donnan potential effects on proton binding equilibria. Protonation behavior of fulvic acids was found to be always directly related to its polyelectrolyte nature and its functional group heterogeneity. A large change in apparent pK_H of the humic substances was observed with degree of neutralization (α) during titration with base, indicating that the various acidic sites that comprise the humic substances were sufficiently different in acid strength. This observation was also confirmed by our experiments. Figure 5 illustrates the change of apparent pK_M with log C_M at different pH. We used the following definition of apparent pK_M:

$$K_M^{app} = \frac{\sum[ML_i]}{[M]\sum[L_i]} \tag{15}$$

Marinsky et al. used the displacement of plots of apparent pK_H versus α as a function of ionic strength for electrostatic correction. The capability to estimate the nonideality contributions to the apparent pK_H has permitted the assignment of four pairs of abundance and intrinsic pK_H values related to four types of binding sites. These intrinsic pK_H values were constant, in the absence of metal ions, for different ionic strength.

CONCLUSIONS

The pH-dependent model represents a more chemically realistic model than the previous pH-independent model. This model should more accurately predict metal–humic complexation reactions that occur in the environment. It should be pointed out that the binding of Eu^{3+} itself to humic substances is not of primary interest. The Eu^{3+} ion is used only as a sensitive probe for measuring the binding of other cations to the humic substances. The single most important conclusion drawn from this study was that this model could be used to predict the thermodynamic binding constant of a single metal species in the complexed humic substance and not conditional binding constants that are usually predicted.

In theory, this model should hold for all pH conditions. At higher pH, however, the formation of metal hydroxides will interfere with the ability to differentiate between bound metal–humic complexes and metal–hydroxide complexes. At very low pH conditions very little metal is bound and it becomes extremely difficult to make accurate ratio measure-

ments over the range of metal concentrations. A compromise of intermediate pH conditions must be made.

LITERATURE CITED

(1) Fish, W.; Dzombak, D. A.; Morel, F. M. M. *Environ. Sci. Technol.* **1986**, *20*, 676–683.
(2) Sposito, G. *CRC Crit. Rev. Environ. Control* **1986**, *16*, 193–229.
(3) Turner, D. R.; Varney, M. S.; Whitfield, M.; Mantoura, R. F. C.; Riley, J. P. *Geochim. Cosmochim. Acta* **1986**, *50*, 289–297.
(4) Cabaniss, S. E.; Shuman, M. S.; Collins, B. J. *Complexation of Trace Metals in Natural Waters*; Kramer, C. J. M., Duinker, J. C., Ed.; Junk Publishers: The Hague, 1984; pp 239–273.
(5) Dobbs, J. C.; Susetyo, W.; Knight, F. E.; Castles, M. A.; Carreira, L. A.; Azarraga, L. V. *Anal. Chem.* **1989**, *61*, 483–488.
(6) Posner, A. M. *8th Int. Congress Soil Sci.* **1964**, 161.
(7) Posner, A. M. *J. Soil Sci.* **1966**, *17*, 65–78.
(8) Perdue, E. M.; Lytle, C. R. *Environ. Sci. Technol.*, **1983**, *17*, 654.
(9) Perdue, E. M.; Reuter, J. H.; Parrish, R. S. *Geochim. Cosmochim. Acta* **1984**, *48*, 1257–1263.
(10) Leenheer, J. A.; Wilson, M. A.; Malcolm, R. L. *Org. Geochem.* **1987**, *11*(No. 4), 273–280.
(11) Horrocks, W. DeW.; Ailbin, M. *Progress in Inorganic Chemistry*; Wiley: New York, 1984; Vol. 31.
(12) Mason, S. F.; Peacock, R. D.; Stewart, B. *Chem. Phys. Lett.* **1974**, *29*, 149.
(13) Cabaniss, S. E.; Shuman, M. S. *Geochim. Cosmochim. Acta* **1987**, *52*, 185–193.
(14) Dzombak, D. A.; Fish, W.; Morel, F. M. M. *Environ. Sci. Technol.* **1986**, *20*, 669–675.
(15) Marinsky, J. A.; Ephraim, J. *Environ. Sci. Technol.* **1986**, *20*, 349–353.
(16) Ephraim, J.; Alegret, S.; Mathuthu, A.; Bicking, M.; Malcolm, R. L.; Marinsky, J. A. *Environ. Sci. Technol.* **1986**, *20*, 354–366.
(17) Ephraim, J.; Marinsky, J. A. *Environ. Sci. Technol.* **1986**, *20*, 367–376.

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